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Sulfur Speciation and Extraction in Jet A

16 August 2015

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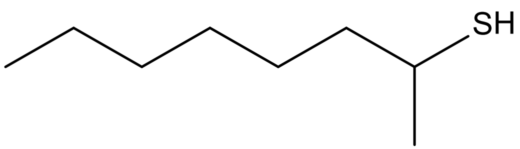
Outline

- Background
- Experimental Setup
  - Extraction of sulfur compounds from fuel to alcohol/water extraction fluid
  - Each rinse is continuous mixing followed by phase separation
  - Multiple rinses, each with fresh extraction fluid
- Results and Conclusions
  - Sulfur levels after each rinse determined by GC-SCD analysis
  - Components grouped by elution times and removal rates compared
  - Regressions applied to predict required number of rinses to meet 15 ppm threshold
  - Extraction efficiencies were different across compound spectrum

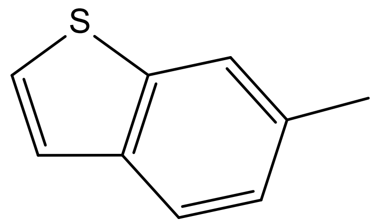
Background

- Example sulfur compounds present in Jet A:

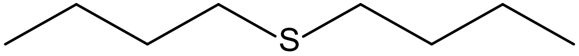
Mercaptans (Thiols)



Thiophenes
and Benzothiophenes



Sulfides



- Detrimental to engine performance: coking, clogging, fouling, and deposits possible
- SO_x emissions are an environmental concern

Experimental Setup

- Materials and Data Sources
  - Extraction fluid: denatured ethanol from Fisher Scientific and deionized water
  - Jet A fuel, approximately 500-800 ppm sulfur by weight
  - Data collected with Agilent Technologies 6890N Gas Chromatography System and Agilent Technologies 355 Sulfur Chemiluminescence Detector attachment
- Method of Analysis
  - GC-SCD tests per ASTM D 5623 with slight edits to meet application-specific requirements
  - Calibration of SCD using known-concentration, single-component sulfur compound standards
  - Samples of treated Jet A taken after 1, 2, 3, 4, and 5 consecutive rinses and compared with untreated Jet A
  - Resulting chromatograms analyzed as 7 distinct sections and collectively

Extraction Apparatus

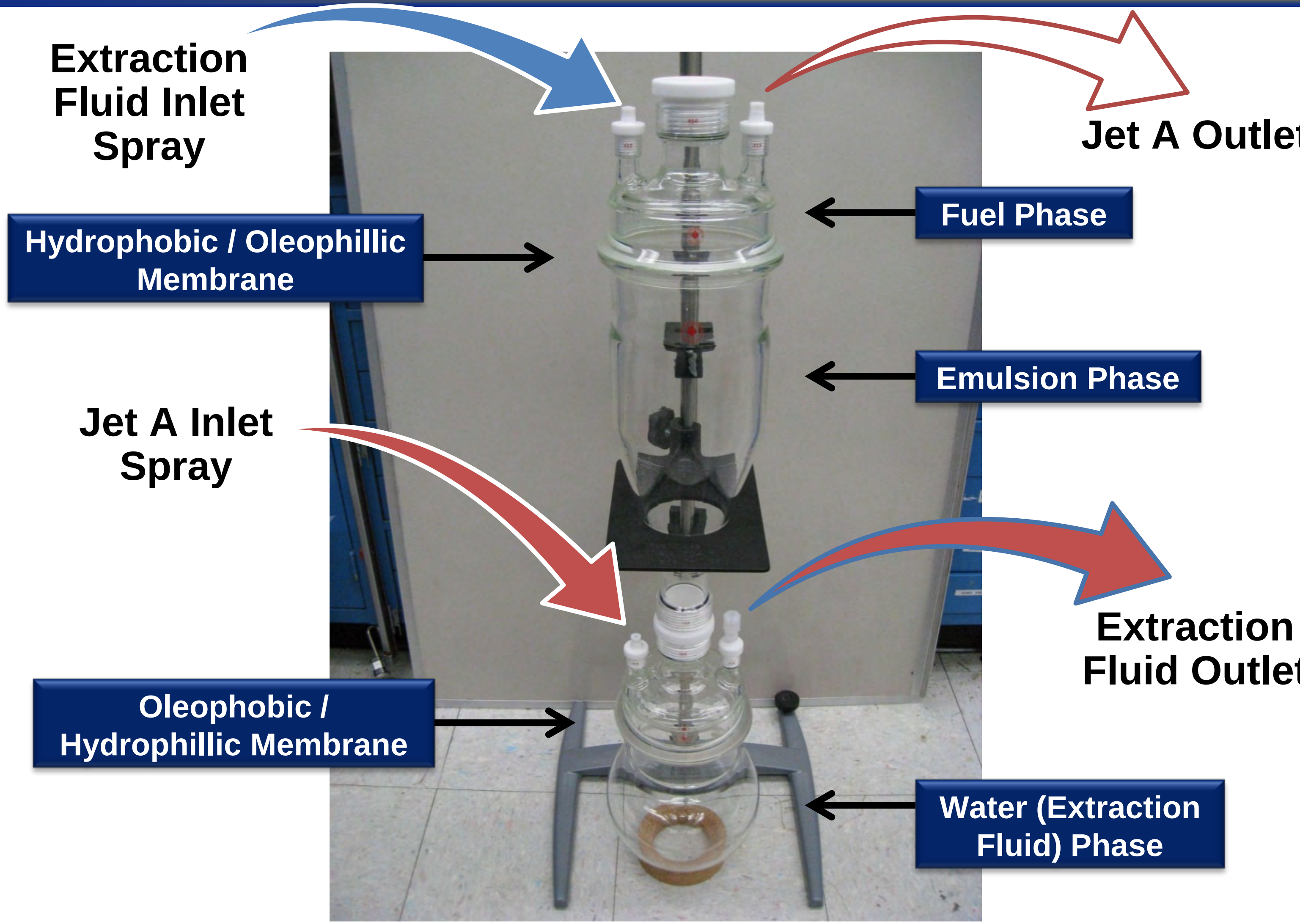


Figure 1

Sulfur Chemiluminescense Detector

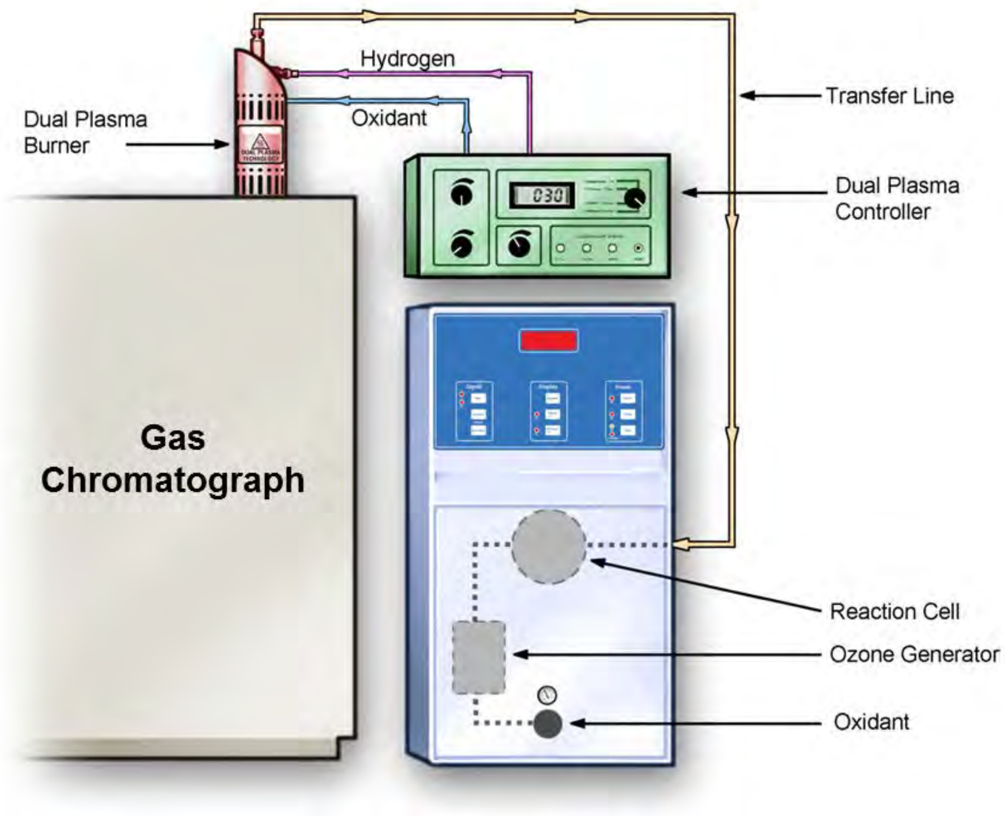


Figure 2

Sulfur compound $\rightarrow$ $SO + H_2O$ + other products

$SO + O_3 \rightarrow SO_2 + O_2 + hv$

Typical Jet A Chromatogram

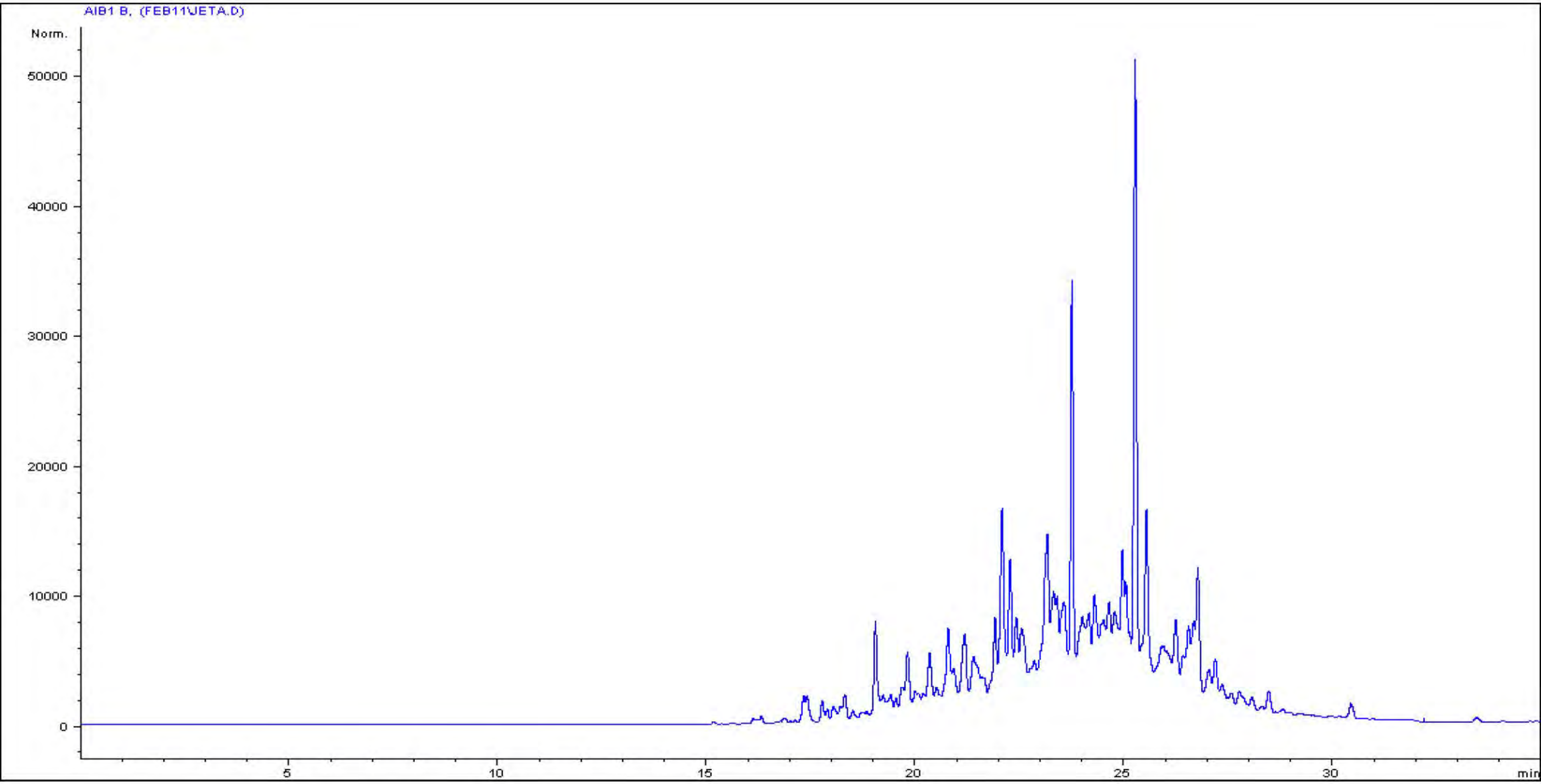


Figure 3

Rinsed Jet A Chromatogram Overlay

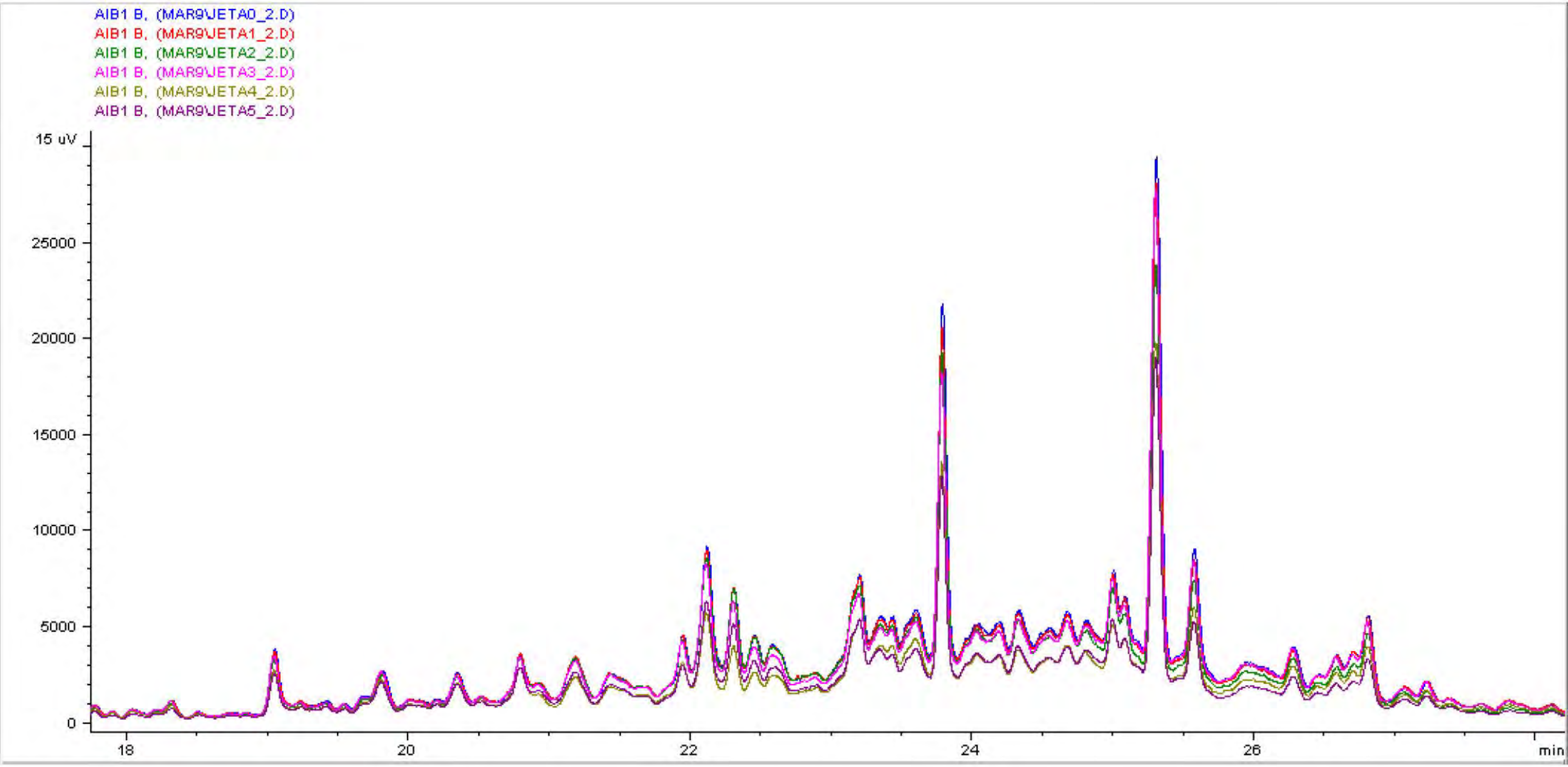


Figure 4

Relevant Calibration Standards

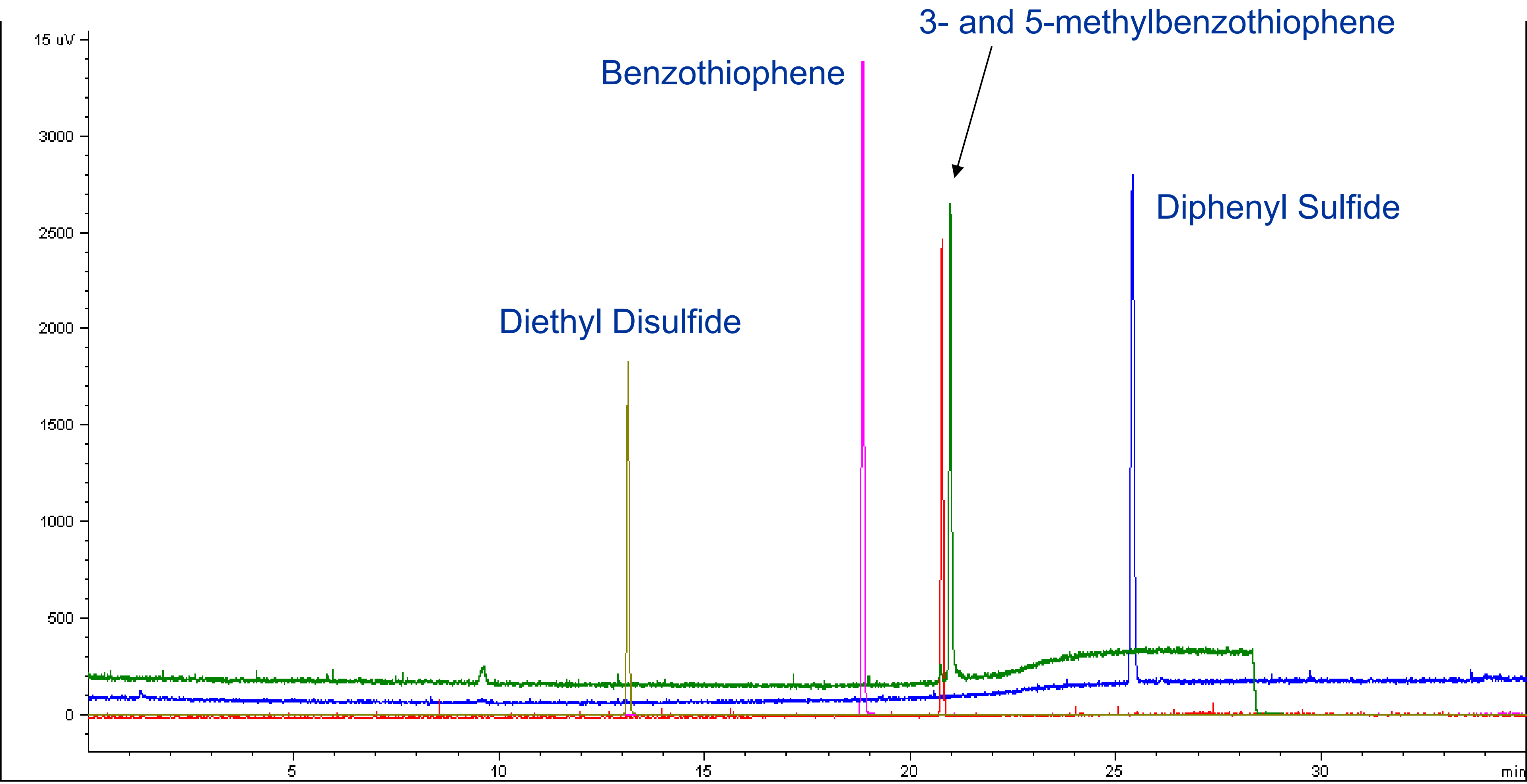


Figure 5

Partition of Jet A Chromatogram

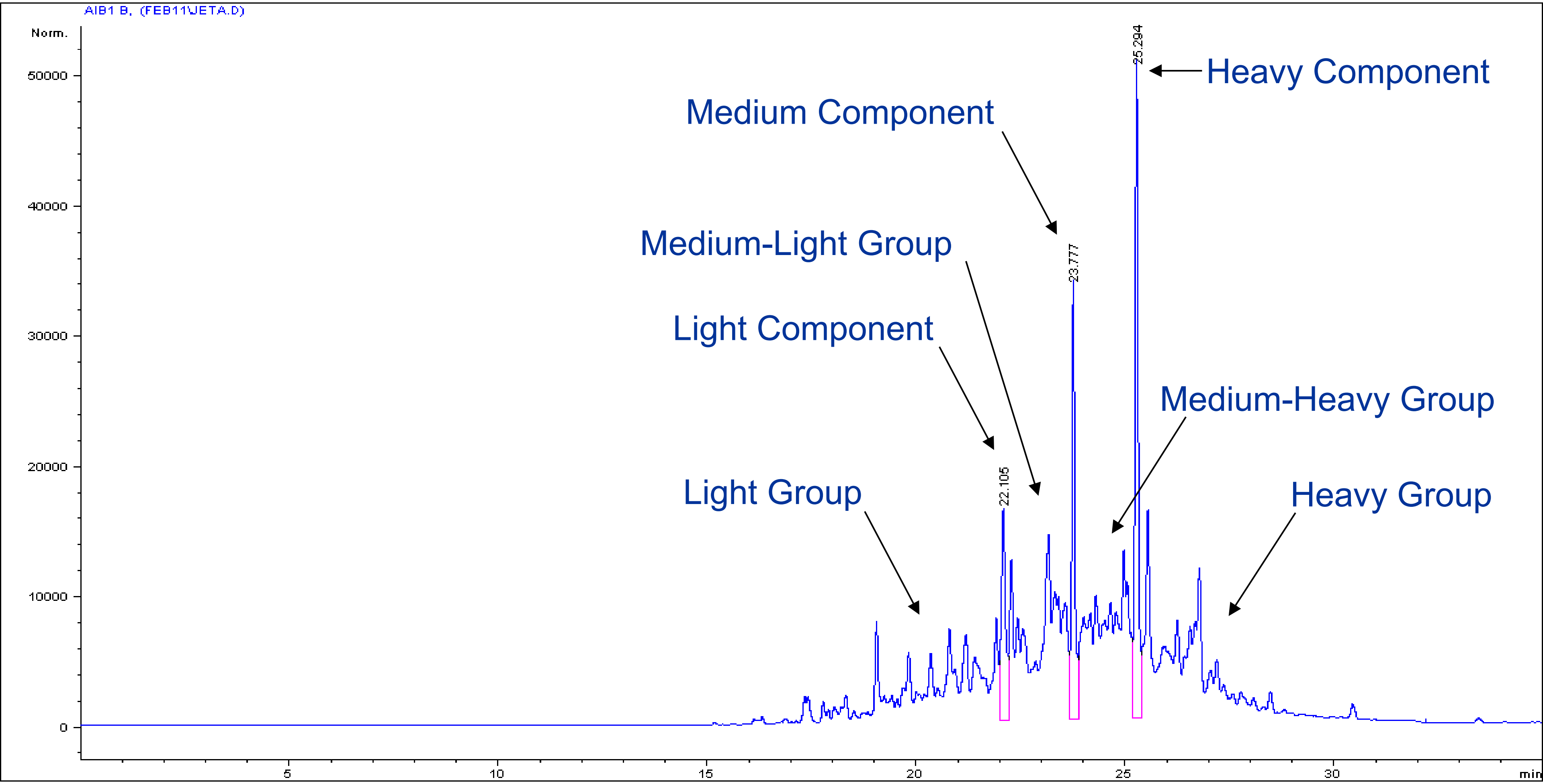


Figure 6

Benzothiophene Calibration Curve

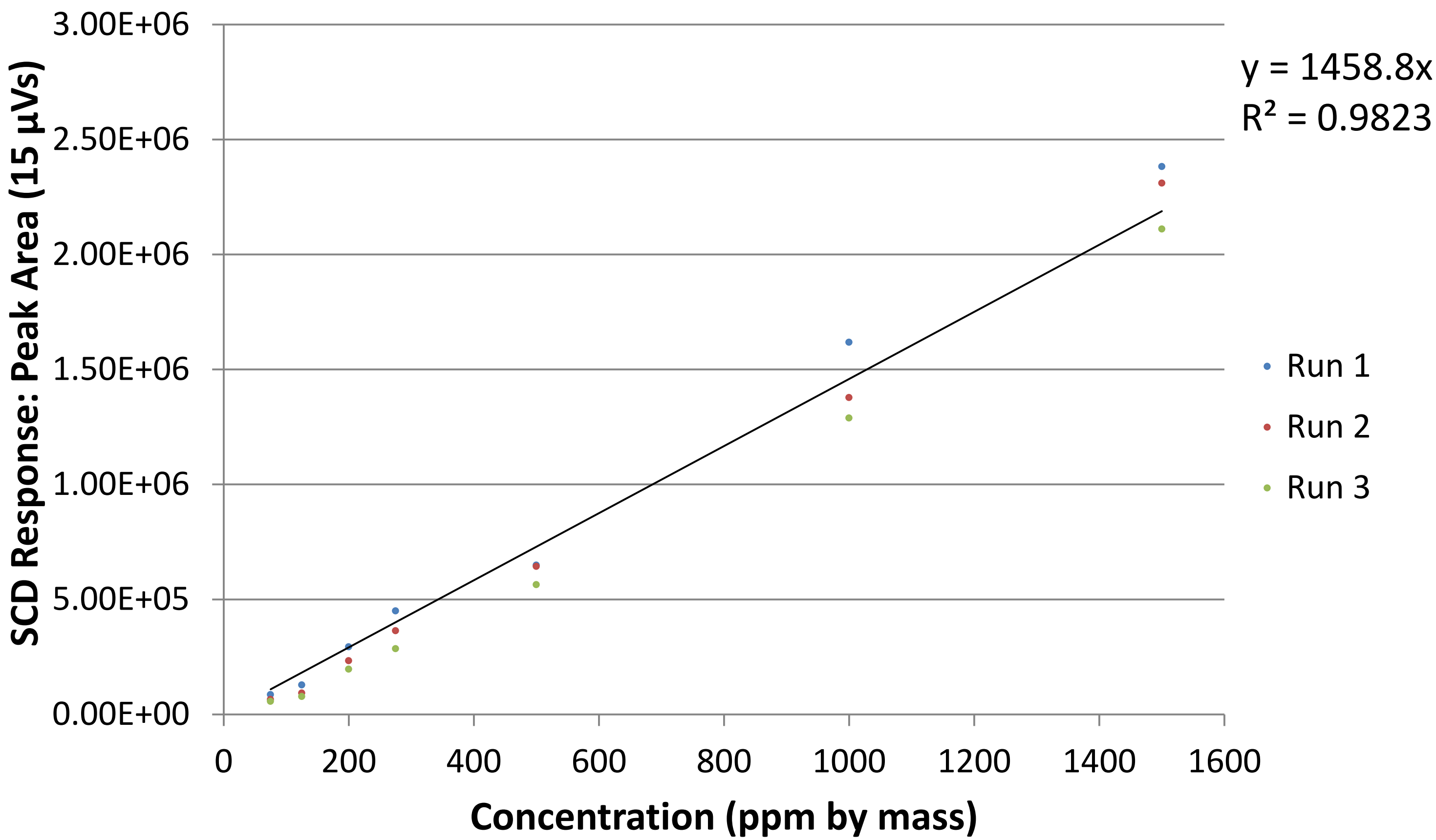


Figure 7

Methylbenzothiophene Calibration Curve

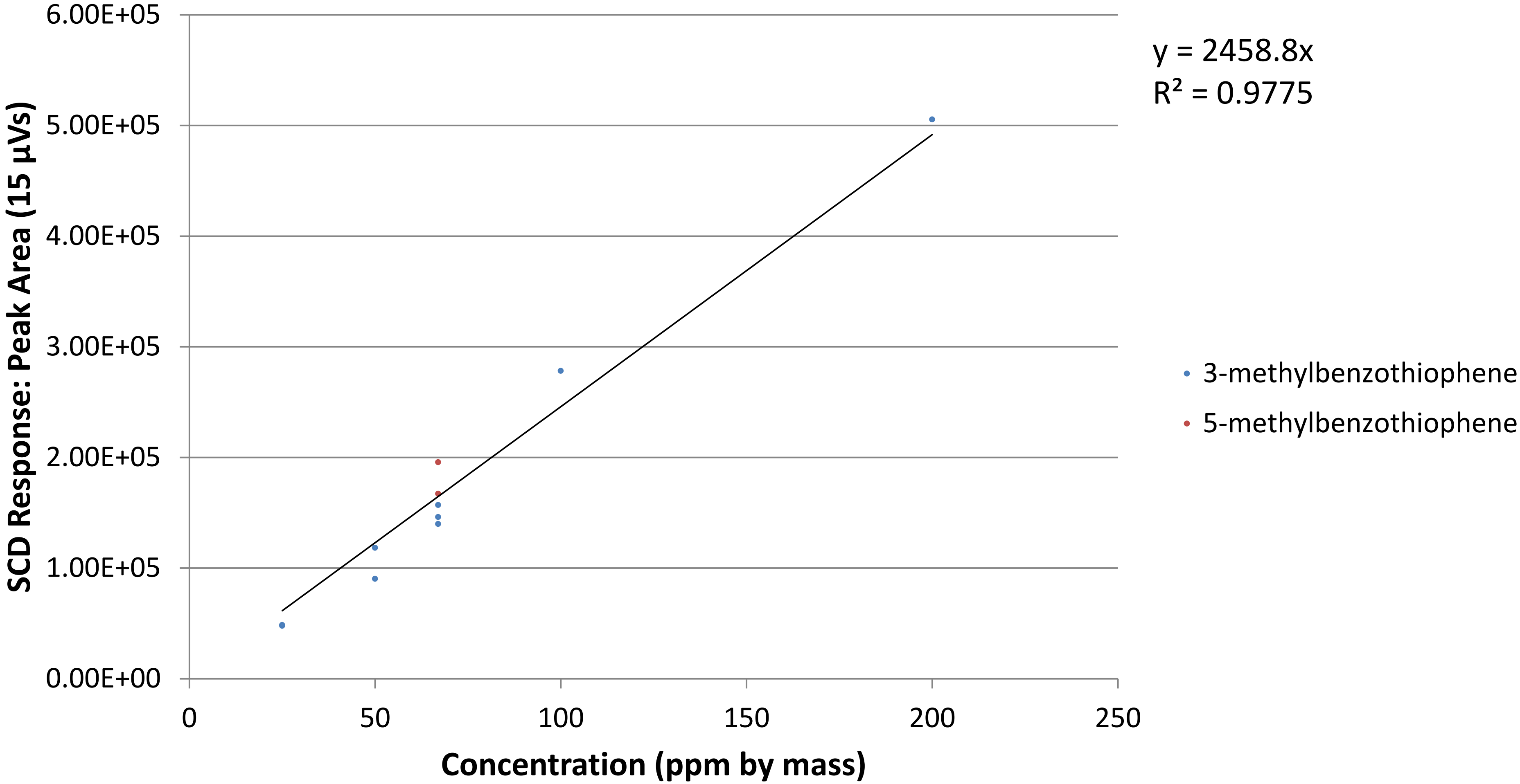


Figure 8

Diphenyl Sulfide Calibration Curve

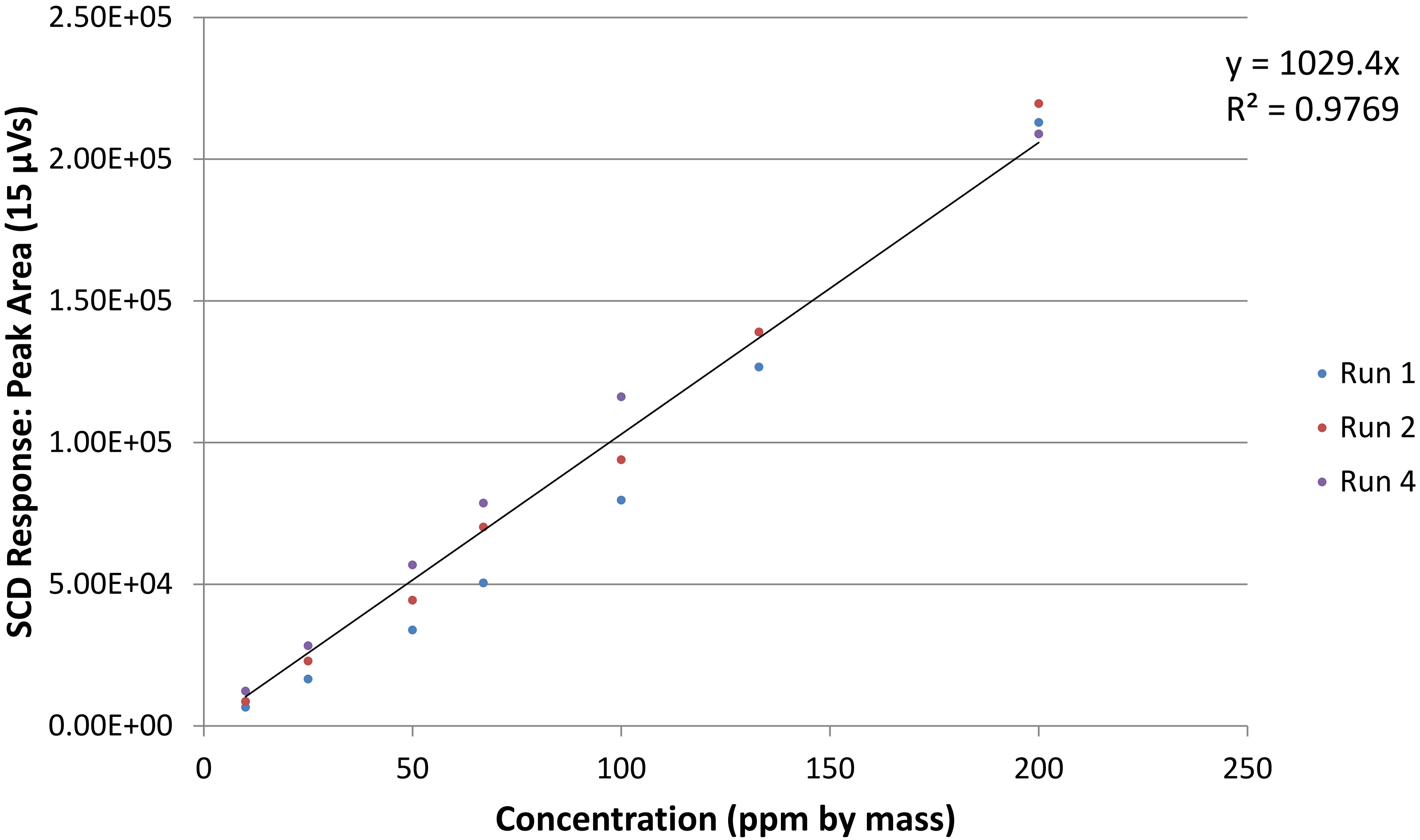


Figure 9

Light (Benzothiophene-like) Group Extraction Profile

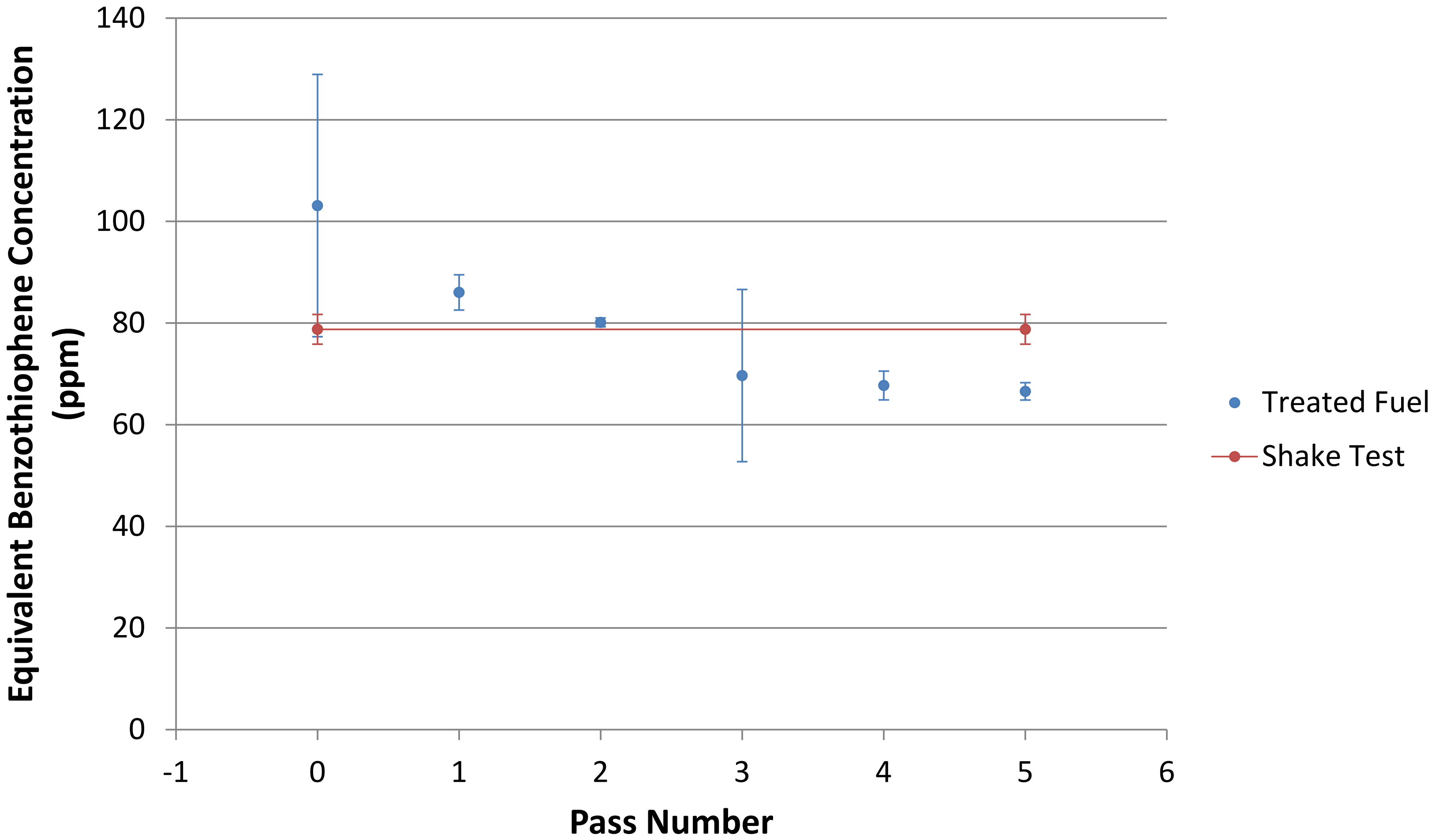


Figure 10

Heavy (Diphenyl Sulfide-like) Component Extraction Profile

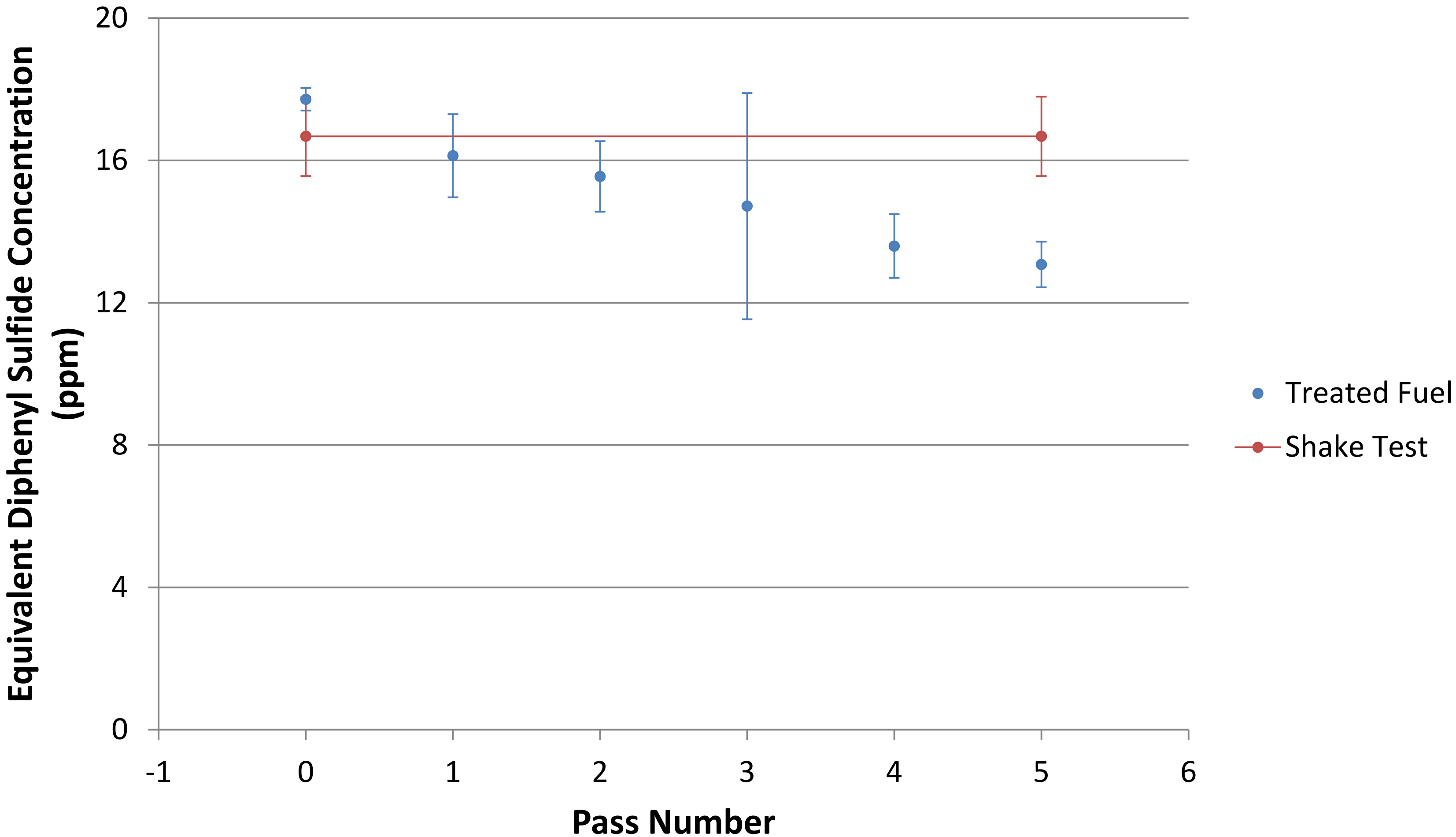


Figure 11

Overall Extraction Profile

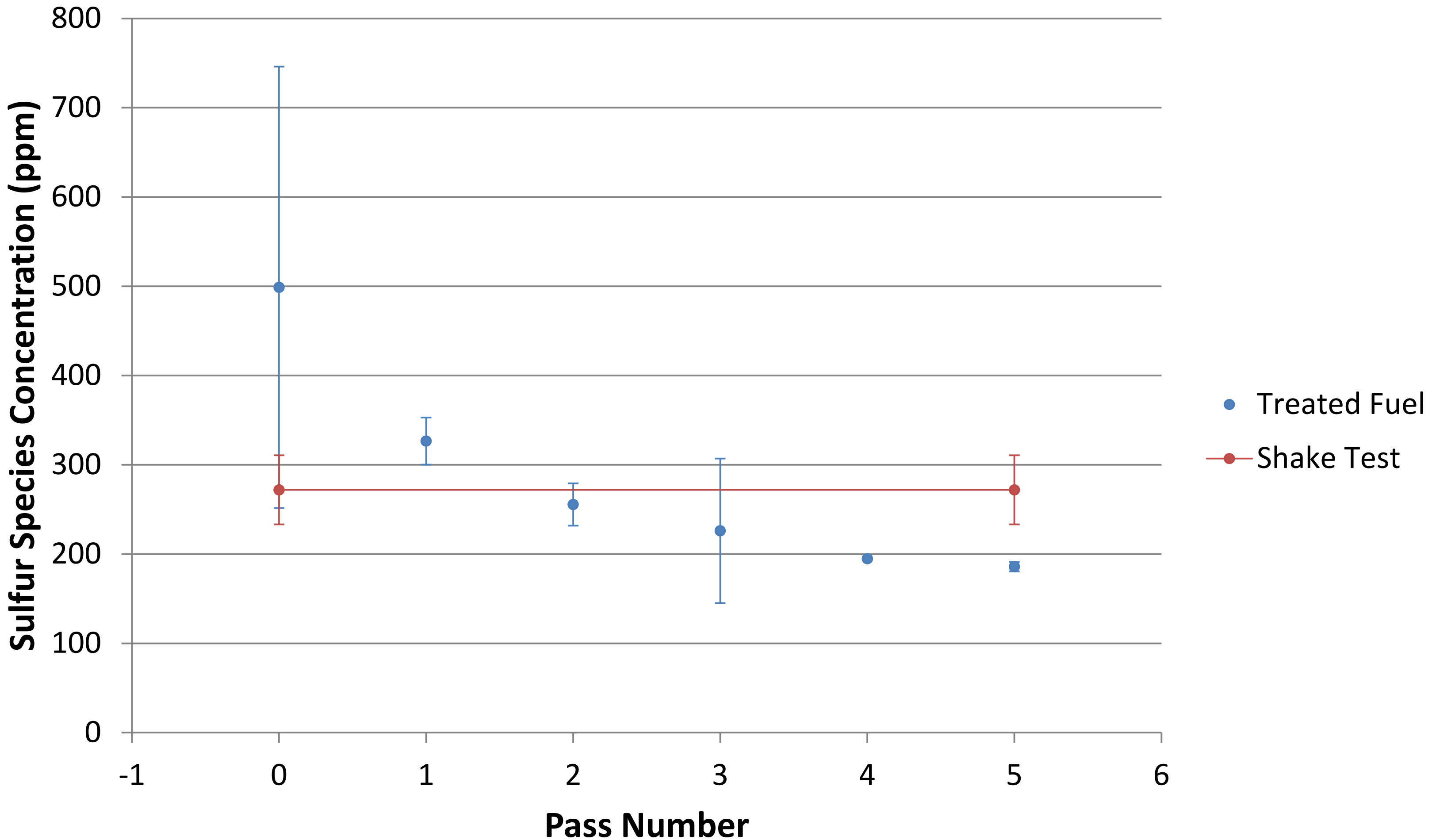


Figure 12

Select Regression Results

	Shake Test Raffinate Ratio	Standard Error	$\overline{R}^2$	Stages Required for 15 ppm Sulfur	95% Upper Limit	95% Lower Limit
Light Component	0.82	0.039	0.92	68	110	26
Medium Component	0.60	0.99	0.87	51	71	32
Heavy Component	0.94	0.015	0.98	94	114	73
Light Group	0.76	0.058	0.88	69	109	28
Medium-Light Group	0.25	0.28	0.87	14	21	8
Medium-Heavy Group	0.86	0.10	0.86	31	42	19
Heavy Group	0.82	0.21	0.52	26	87	5
Total	0.55	0.13	0.88	34	47	20

Table 1

Extraction Models

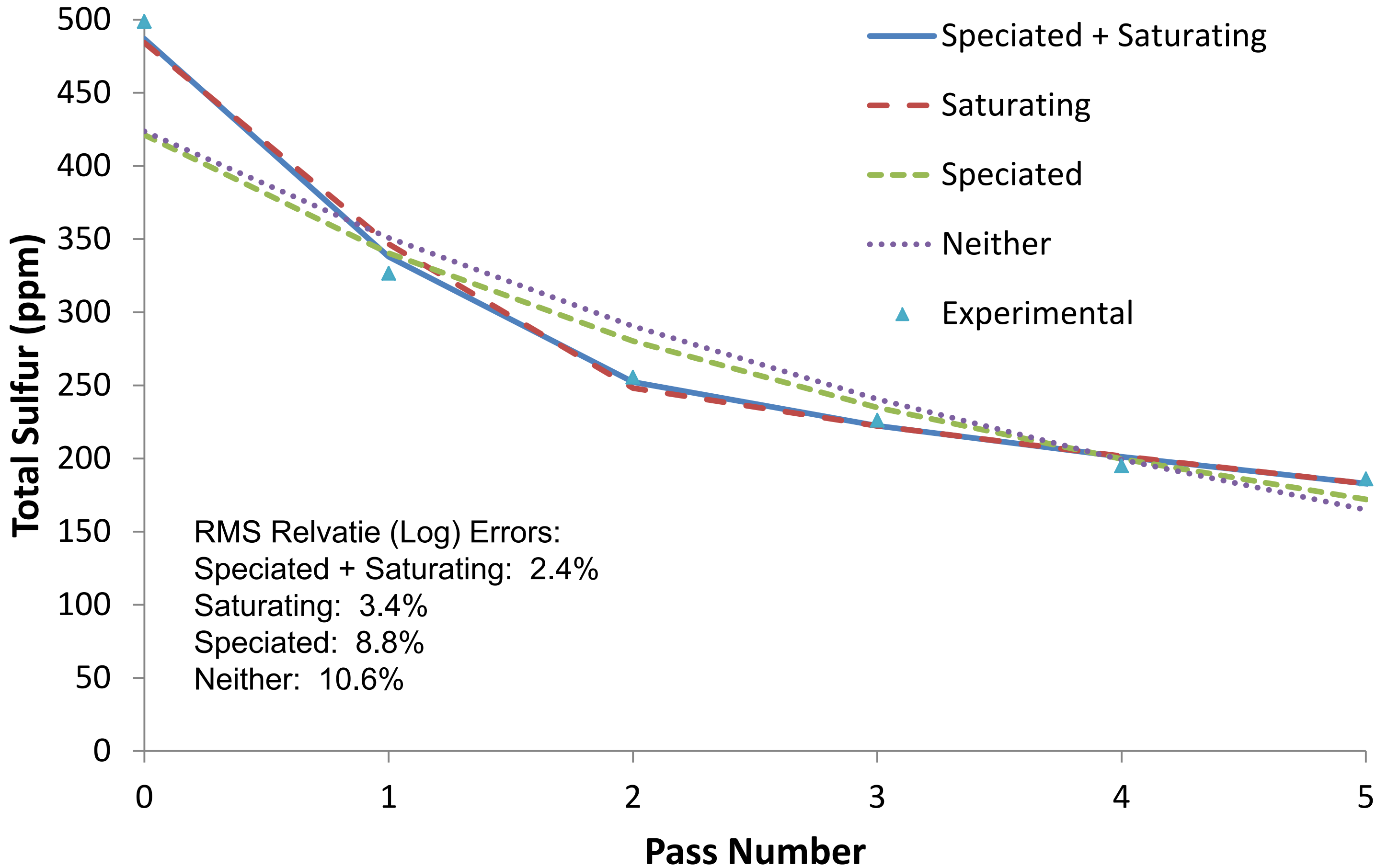


Figure 13

Extraction Models

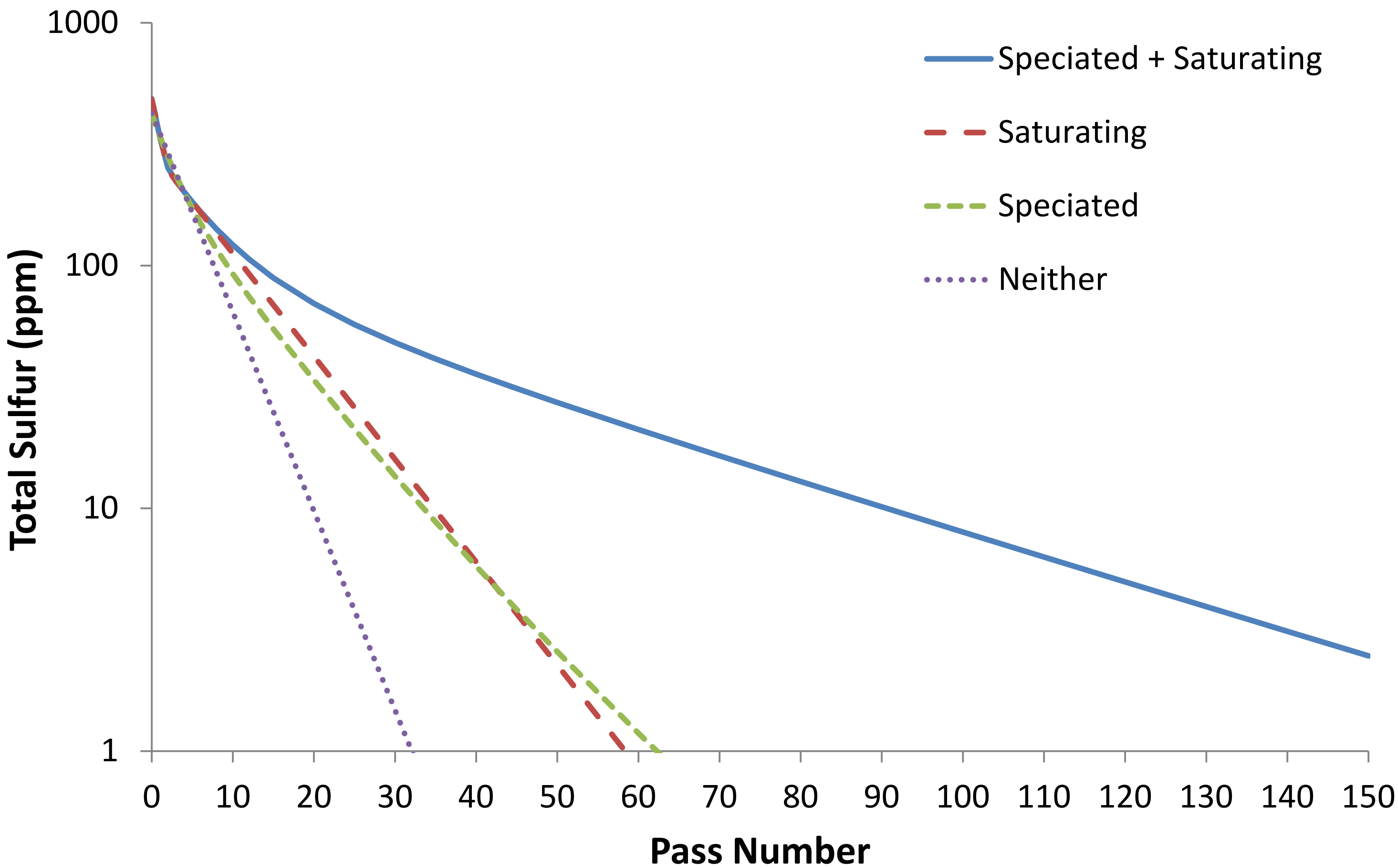


Figure 14

Summary

To analyze sulfur content, GC-SCD was used. Calibration standards were developed to relate signal output of the device to sulfur concentration, and this relation was then used to quantify the sulfur in samples of Jet A. Samples of the fuel were tested prior to rinsing and after up to 5 consecutive rinses. With consecutive alcohol/water extraction fluid rinses, the sulfur content of Jet A fuel was shown to be reduced significantly.

The resulting Jet A chromatograms were partitioned into seven components and groups to study relative rates of extraction. It is apparent that the spectrum of sulfur-containing compounds in Jet A are not removed at the same rate; generally, the lighter components (those with lower elution times) are more prone to removal than the heavier ones. Saturation also appears to be occurring, restricting extraction efficiency further, especially in higher quantities of consecutive rinses.